

The occurrence of inorganic elements in various biofuels and its effect on combustion behavior

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The Pennsylvania State University is performing a feasibility analysis on installing a state-of-the-art circulating fluidized bed (CFB) boiler and ceramic filter emission control device at Penn State's University Park campus for cofiring multiple biofuels and other wastes with coal. This effort, in combination with a variety of agricultural and other wastes generated at the agricultural-based university and the surrounding rural community, has led Penn State to assemble a team of fluidized bed and cofiring experts to perform the feasibility study. The team includes personnel from Penn State's Energy Institute, the Office of Physical Plant, and the College of Agricultural Sciences; Foster Wheeler Energy Services, Inc; and Cofiring Alternatives.

A resource characterization has been completed in which the types and quantities of potential feedstocks have been assessed. Approximately twenty different biomass, animal waste, and other wastes were identified, collected and analyzed. Of these feedstocks, chemical fractionation analysis was performed on eleven of the major streams to assess the potential for bed agglomeration and superheater corrosion for a given cofire blend. For the purposed of this paper, the Reed Canary grass, sheep and dairy tie-and free-stall manure, miscellaneous manure, poultry litter, and pine shavings will be discussed. Analysis of selected biomass materials is given in Table 1.

This paper reports the chemical fractionation results for seven biofuels. Chemical occurrence is classified as water soluble/ion-exchangeable, acid soluble and insoluble for K, Na, Ca, Mg, Si, Al, P, S and Fe. An example of chemical fractionation data presented in the paper is given in Figure 1. A detailed chemical fractionation methodology is presented that addresses the extremely heterogeneous character of the various components that constitute a biofuel. Results of the chemical fractionation data indicate that 90% of the potassium and sodium in the fuels is present in a water-soluble and/or ion-exchangeable form. Calcium in the fuels is either present in a water soluble/ion-exchangeable form or acid soluble form. Iron is associated in the acid soluble form. Phosphorous is present in a water soluble/ion-exchangeable form. Aluminum and silicon remain in the insoluble portion of the fuel attributed to the presence of straw and dirt from the floor of dairy and poultry barns.

Thermodynamic equilibrium modeling via FactSage on a series of fuel blends (Table 2) indicated that biofuel blends cofired with a low-fouling coal (Baseline Blend and Manure-Coal Cofire) do not form significant liquid phases at temperature characteristic of circulating fluid bed combustors (CFBs) (1171K) if the coal used provides a significant portion of the thermal input. Biofuels containing little aluminum and minor potassium (as little as 0.02 mass fraction K_2O normalized with respect to SiO_2 and Al_2O_3) tend to form liquid $K_2Si_4O_9(l)$ at 1171K (Manure Blends 1 and 2). The mass fraction of $K_2Si_4O_9(l)$ formed is also very sensitive to the mass fraction of Al_2O_3 present. An increase in Al_2O_3 with respect to SiO_2 and Al_2O_3 resulted in the formation of aluminosilicates and potassium aluminosilicates having higher melting points. The poultry litter fuel formed $NaSO_4(l)$ at 1171K. Pilot-scale tests conducted at Penn State and modeling studies showed that the $NaSO_4(l)$ can be mitigated with the addition of aluminum via the addition of kaolin clay.

Table 1. Proximate, ultimate and ash analysis of cofire coal and biomass fuels

	Cofire Coal	Pine Shavings	Reed Canary Grass	Sheep Manure	Dairy Free-Stall Manure	Dairy Tie-Stall Manure	Misc. Manure	Poultry Litter
Moisture	5.0	45.0	65.2	47.8	70.3	69.8	50.5	20.0
Proximate analysis (wt.%, db)								
Volatile matter	24.16	84.7	76.1	65.2	30.6	30.1	21.8	55.3
Ash	14.70	0.1	4.1	20.9	62.3	62.5	73.5	17.0
Fixed carbon	61.14	15.2	19.8	14.0	7.1	7.4	4.8	7.7
HHV (Btu/lb, db)	13,118	8,373	7,239	6,895	3,799	8,203	3,114	6,399
Ash Analysis (wt.%)								
Al ₂ O ₃	25.34	13.4	1.66	3.08	0.96	2.26	1.34	9.14
BaO	--	0.15	0.05	0.05	0.02	0.02	0.01	0.05
CaO	2.28	8.75	9.57	12.8	6.38	23.3	3.44	12.7
Fe ₂ O ₃	18.34	5.94	1.47	1.95	1.29	1.37	0.93	4.04
K ₂ O	2.22	4.94	18.1	23.4	6.75	10.7	1.77	9.94
MgO	0.82	3.35	5.29	5.74	2.65	8.91	1.06	4.01
MnO	--	0.49	0.11	0.17	0.17	0.14	0.03	0.36
Na ₂ O	0.25	1.38	2.34	4.64	1.32	7.04	0.88	3.60
P ₂ O ₅	0.4	1.44	13.8	9.21	2.90	14.7	2.54	14.0
SiO ₂	48.2	57.2	43.0	29.3	74.98	26.0	84.82	39.4
SO ₃	0.67	0.05	0.02	5.52	0.04	0.14	0.01	2.58
SrO	--	0.80	0.11	0.03	0.10	0.11	0.14	0.03
TiO ₂	--	1.16	4.99	0.20	2.06	5.08	1.20	0.51

Figure 1. Occurrence of potassium in biofuels (example of chemical fractionation data)

Table 2. Fuel blends used for thermodynamic modeling study.

% Thermal Input					
Fuel	Baseline Blend	Chicken Litter	Manure Blend 1	Manure Blend 2	Manure-Coal Cofire
Coal	83.8				84.9
Sewage Sludge	0.4				
Sheep Manure	0.1		59.0	25	3.9
Chicken Litter	0.0	100			
Dairy Tie-Stall Manure	0.4		21.5	25	4.0
Dairy Free-Stall Manure	0.0		8.1	25	3.4
Misc. Manure	0.3		11.7	25	3.9
Red Oak Shavings	8.4				
Pine Shavings	6.5				
Reed Canary Grass	0.2				